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Band gap and Schottky barrier heights of multiferroic BiFeO₃

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BiFeO₃ is an interesting multiferroic oxide and a potentially important Pb-free ferroelectric. However, its applications can be limited by large leakage currents. Its band gap is calculated by the density-functional based screened exchange method to be 2.8 eV, similar to experiment. The Schottky barrier height on Pt or SrRuO₃ is calculated in the metal induced gap state model to be over 0.9 eV. Thus, its leakage is not intrinsic. © 2007 American Institute of Physics.
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There is increasing interest in materials which display simultaneous ferroelectric and magnetic properties, the multiferroics,^{1–5} of which BiFeO₃ is the best known example. It was noted that the remnant polarization of bulk BiFeO₃ of 3.5 $\mu\text{C}/\text{cm}^2$ was low compared to its high Curie temperature.⁶ Recently, Wang *et al.*⁷ and Eerenstein *et al.*⁸ found that thin epitaxial films of BiFeO₃ on SrTiO₃ substrates displayed much higher polarizations of $\sim 90 \mu\text{C}/\text{cm}^2$ and this is becoming accepted as the bulk value.^{5,9} There is also an interest in Pb-free ferroelectrics such as BiFeO₃ for environmental reasons.¹⁰ These observations suggest a number of possible applications of BiFeO₃ thin films in high-density data storage, etc. However, these films often show sizable electrical leakage currents.^{11–16} These can mask measurements of the polarization loop and could short-circuit ferroelectric storage devices, so there have been extensive efforts to reduce the leakage currents.^{14–16} It is therefore of interest to know the band gap of BiFeO₃ and its conduction mechanisms, in order to know if the leakage is intrinsic or extrinsic.

On the theory side, the atomic structure and multiferroic character of BiFeO₃ and related materials can be partially described by the local spin density approximation (LSDA) of the local density approximation (LDA). However, LDA is known to underestimate the band gap for semiconductors. LSDA is well known to be particularly poor for correlated insulators, of which NiO is the classic case.¹⁷ LDA gives a metal, whereas experimentally it has a 4 eV band gap.¹⁸ For BiFeO₃, LSDA gives a rather small band gap of 0.3–0.77 eV.^{19,20} If this were true, it would lead to a very high leakage current.

This problem can be corrected by using density-functional methods which go beyond LDA. The simplest of these is “LDA+U” in which an empirical on-site potential (U) is added to the atomic (pseudo-) potential.²¹ This method was employed by Neaton *et al.*¹⁹ for BiFeO₃, who found band gaps from 0.3 to 1.9 eV, depending on the value of U. The most accurate but expensive method is the parameter-free GW approximation.²² Here, we calculate the electronic structure of BiFeO₃ using the screened exchange (sX) method.^{23–26} This is a parameter-free, density-functional method of including an improved electronic exchange poten-

tial, but it is less expensive than GW. The sX method has been found to give good band gaps for many insulating oxides and semiconductors.^{25,26} We then use this band structure to calculate the Schottky barrier height of various metals on BiFeO₃ and thus find the likely size of any intrinsic leakage currents.

Our calculations use the CASTEP plane-wave pseudopotential code.²⁷ The sX potential is a density-functional method based on Hartree-Fock, which includes the electron exchange via a Thomas-Fermi screened exchange term.²³ The sX potential is actually a true energy functional which could be used to minimize the total energy. However, for speed reasons, here we calculate the atomic structure by the conventional spin-polarized generalized gradient approximation, and then use sX to calculate the energy bands from this structure. Norm-conserving pseudopotentials are used and the plane-wave cutoff energy is 800 eV.

BiFeO₃ is a perovskite whose most stable phase is the *R3c* rhombohedral structure.²⁸ This is a distortion of the basic cubic perovskite structure in which the oxygen octahedra are rotated in alternate senses about the (111) axis, as seen in two projections in Fig. 1. The Bi³⁺ ions are displaced along (111) and this leaves the oxygens effectively fourfold coordinated to two Bi³⁺ ions and two Fe³⁺ ions. BiFeO₃ has an antiferromagnetic ordering, with the spins on the Fe³⁺ ions being aligned in opposite senses along the (111) axis.

Our calculated structural parameters are similar to those of Neaton *et al.*¹⁹ The resulting bands in sX are shown in

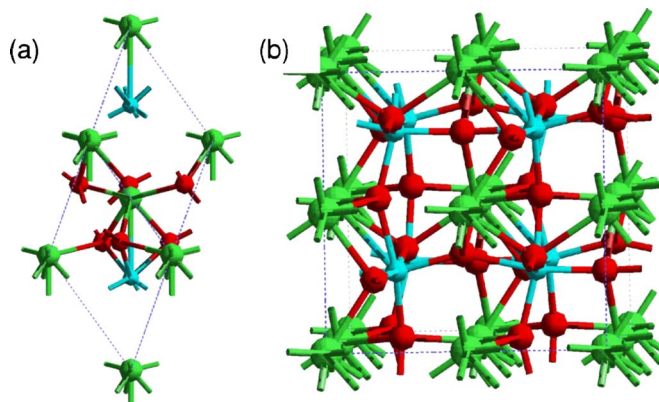


FIG. 1. (Color online) Structure of the *R3c* phase (a) rhombohedral cell and (b) pseudocubic cell. Oxygen=red, Bi=green, and Fe=blue.

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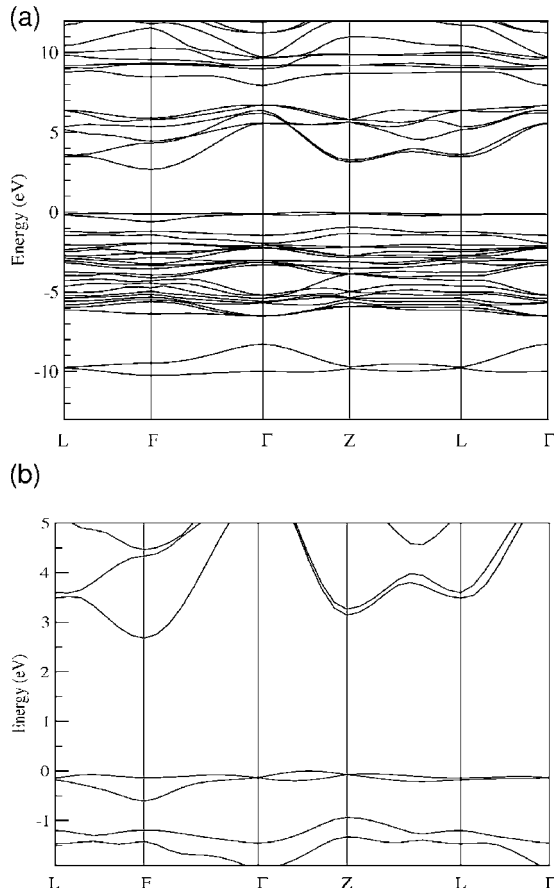


FIG. 2. (a) Spin polarized band structure of antiferromagnetic BiFeO₃ and (b) closeup of the bands near the band gap.

Fig. 2. Figure 2(b) shows a closeup of the bands near the gap. The partial density of states (DOS) is shown in Fig. 3. The top of the valence band is set at 0 eV. In Fig. 3, the lowest bands at -10 eV are due to Bi 6s states mixing with some O *p* states. There then follows a broad mass of bands above -7 eV due to hybridized O *p* and Fe *d* states. The Fe *d* states continue in the conduction band above the gap and there then follow the Bi 6*p* states above 4 eV. The Fe density of states is quite different for the two spin states, as found by Neaton *et al.*¹⁹ The Fe-O bond is quite polar, so the O *p* states lie mainly in the valence band.

The calculated band gap is 2.8 eV. The band gap is zero for the cubic structure. It requires both the ferroelectric distortion and the spin polarization to open up the gap. The band gap is indirect, from a rather flat band along *FT* in the valence band to a conduction band minimum at *F*.

Our band gap of 2.8 eV compares to an experimental gap of about 2.5 eV from the optical absorption spectra by Kanai *et al.*²⁹ and Gao *et al.*³⁰ The latter was on BFO nanowires but is similar to the bulk value. Our gap of 2.8 eV is larger than that calculated by Neaton *et al.*¹⁹ Gaps of 2.5–2.9 eV would correspond to *U* values of 5–6 eV in the LDA+*U* method, respectively, which are typical for Fe. The similarity of the calculated gap to experimental values suggests that the screened exchange method works well for correlated oxides as well as simple closed shell oxides.

The DOS in Fig. 3 shows that the Bi³⁺ ion retains its 6s electrons, and the lone pair does lie off center for this site. However, the ferroelectricity originates from dynamic not static effective charge, so the origin of ferroelectricity in

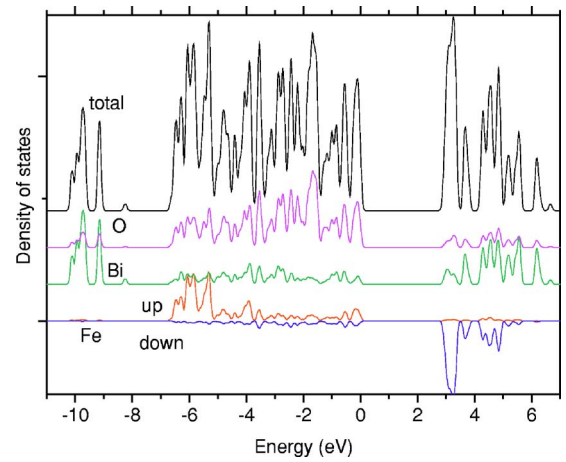


FIG. 3. (Color online) Partial density of states, including spin up and spin down on one of the Fe sites.

these materials is better described as originating from dynamic O *p*–Bi *p* hybridization.

The Schottky barrier height of BiFeO₃ against various metals can be calculated using the model of metal induced gap states (MIGSs). This model treats the component of the barrier height that arises from electronegativity differences and omits the specific interface chemistry. This was previously found to give a reasonable description of the barrier heights of SrTiO₃ and PbTiO₃, as well as other wide gap oxides.³¹ At the interface of a metal and oxide, the metal states decay as evanescent states into the band gap of the oxide. They are occupied up to an energy known as the charge neutrality level (CNL) for a neutral surface. The barrier height depends on charge transfer across the interface between the metal and the oxide's MIGS. The finite density of MIGs acts to pin the Fermi energy towards the CNL according to

$$\phi_n = S(\Phi_M - \Phi_S) + (\Phi_S - \chi_S). \quad (1)$$

Here Φ_M is the metal work function, Φ_S is the CNL of the oxide, χ_S is the electron affinity of the oxide, and *S* is a dimensionless Schottky barrier pinning factor characteristic of the oxide. Each of these parameters is known or can be estimated. χ_S of BiFeO₃ is estimated as 3.3 eV, by comparison with SrBi₂Ta₂O₉ in which the Bi *p* states also form the conduction band. *S* can be estimated from the optical dielectric constant ϵ_∞ of BiFeO₃ using the empirical formula of Mönch,³²

$$S = \frac{1}{1 + 0.1(\epsilon_\infty - 1)^2}. \quad (2)$$

ϵ_∞ is derived from the refractive index of 2.62.³³ This gives $S=0.23$, which compares to $S=0.28$ for SrTiO₃.

The CNL energy of BiFeO₃ can be calculated from the bulk band structure as the energy where the Green's function *G* is zero, using

$$G(E) = \int_{\text{BZ}} \int_{-\infty}^{\infty} \frac{N(E')dE'}{E - E'} = 0. \quad (3)$$

It suffices to replace the integral by a sum over a few special points.³¹

The predicted *n*-type Schottky barriers of various metals on BiFeO₃ are plotted against their vacuum work functions

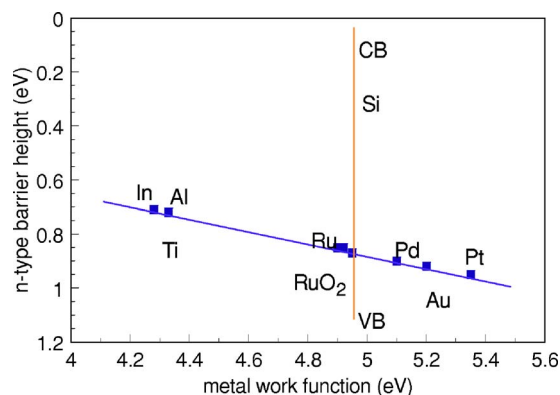


FIG. 4. (Color online) Schottky barrier heights vs metal work functions.

in Fig. 4. This shows that the barrier of Pt will be 0.95 eV. The barrier to a typical conducting oxide RuO_2 or SrRuO_3 would be 0.9 eV. These are sizable energy barriers. Thus overall, the band gap of BiFeO_3 is not as large but approaches that of SrTiO_3 . The barrier heights are sufficiently large to inhibit Schottky emission from the metal into the oxide conduction band, the most likely intrinsic form of conduction.

Experimentally, BiFeO_3 films can show considerable electrical conductivity.^{11–16} It was found that the conductivity could be reduced by optimizing the growth procedures.^{12–16} The conductivity could be greatly reduced by doping the BiFeO_3 with Ti^{4+} ions¹³ or Mn,¹⁶ but increased by doping with NiO.¹³ This suggests that the conductivity originates from oxygen vacancy levels in the oxide band gap. They form rather shallow states in many perovskites. O vacancies occur to allow mixed Fe valence.

Overall, our calculated band gap and Schottky barrier heights for BiFeO_3 are large enough to suggest that electronic leakage can be small. The gap is much larger than found in earlier LSDA calculations and similar to experiment. It suggests that the screened exchange method works well for correlated oxides as well as simple oxides. It suggests that leakage current can be reduced by better processing conditions of the oxide films.

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